Supplementary Material (ESI) for Green Chemistry

Mechanism of Efficient Anti-Markovnikov Olefin Hydroarylation Catalyzed by Homogeneous Ir(III) Complexes

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Warning! Organomercury compounds are highly toxic! There is a danger of cumulative effects. These compounds may cause serious and irreversible effects on skin contact. These compounds may be fatal if absorbed through the skin - even small amounts, such as a single drop, may cause serious injury or potentially be fatal. They may cause metal fume fever if inhaled or swallowed. Chronic exposure may cause irreversible CNS damage, sensitization, weight loss, immunological disease and other serious effects. Work with these dangerously toxic compounds must not begin before a full assessment of the risks has been made and suitable protocols established including reading and understanding available safety information (MSDS).

Experimental Conditions. All manipulations were carried out using glovebox and high vacuum line techniques under an inter atmosphere of N_2 or argon. Benzene, benzene-d_6, toluene-d_8 and THF were purified by vacuum transfer from sodium benzophenone ketyl. CD_2Cl_2 and pyridine were dried by vacuum transfer from CaH_2. Synthetic work involving iridium complexes was carried out in an inert atmosphere in spite of the air stability of the complexes. Reagent-grade chemicals and solvents were used as is and purchased from Aldrich or Strem. $CH_3{}^{13}CH_2I$ was purchased from Cambridge Isotopes Inc. and was used as received. Complexes **R-Ir-L**, **[R-Ir]$_2$** and **cis R-Ir-L,Error! Bookmark not defined.**[i] and diethylmercury[ii] were prepared as described in the literature. Elemental analyses were done by Desert Analytics laboratory; Tucson, Arizona. Liquid phases of the reaction mixtures were analyzed with a Shimadzu GC-MS QP5000 (ver. 2) equipped with cross-linked methyl silicone gum capillary column, DB5. Gas measurements were performed using a GasPro column. The retention times of the products were confirmed by comparison to authentic samples. NMR spectra were obtained on a Bruker AM-360 (360.138 MHz for ^{1}H and 90.566 MHz for ^{13}C), Bruker AC-250 (250.134 MHz for ^{1}H and 62.902 MHz for ^{13}C) or on a Varian Mercury 400 (400.151 MHz for ^{1}H and 100.631 MHz for ^{13}C) spectrometer. Chemical shifts are given in ppm relative to TMS or to residual solvent proton resonances. All carbon resonances are singlets unless otherwise mentioned.

Table S1. Kinetic dependence of hydroarylation on benzene concentration

Benz / [M]	TN
2.8	1.05
5.6	2.445
8.4	3.3
11.2	5.2

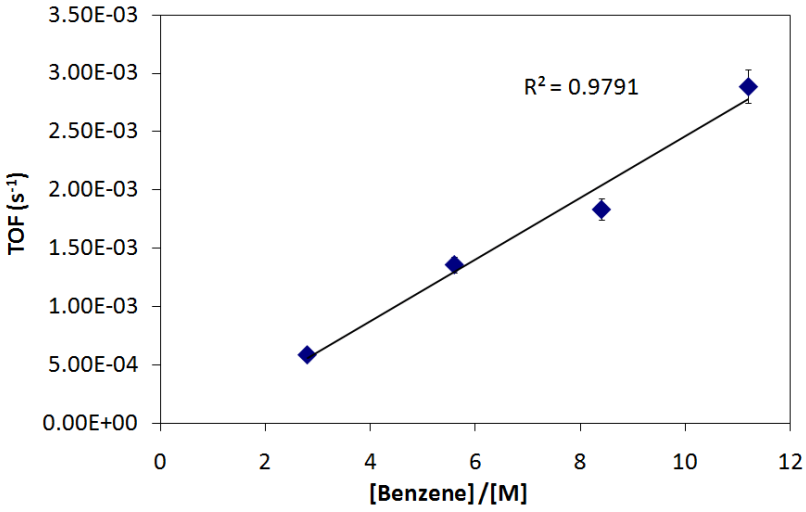

Table S2. Kinetic dependence of hydroarylation on olefin concentration

Styr / [M]	TN
1.454633	1.36
2.493656	2.76
3.272924	5.24
3.879021	2.56
4.363898	1.42

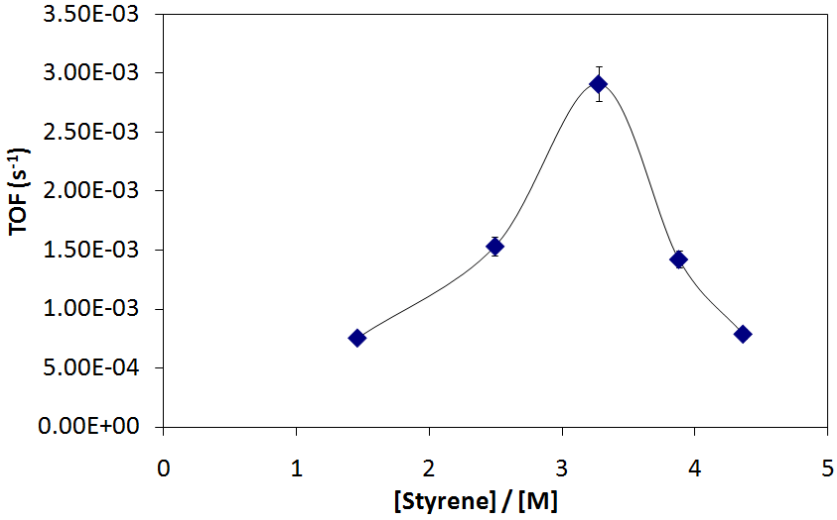

Table S3. Kinetic Dependence of Hydroarylation on Pyridine Concentration

1/Py Eq.	TN
0.37	1.63
0.185	0.81
0.123	0.57
0.093	0.49

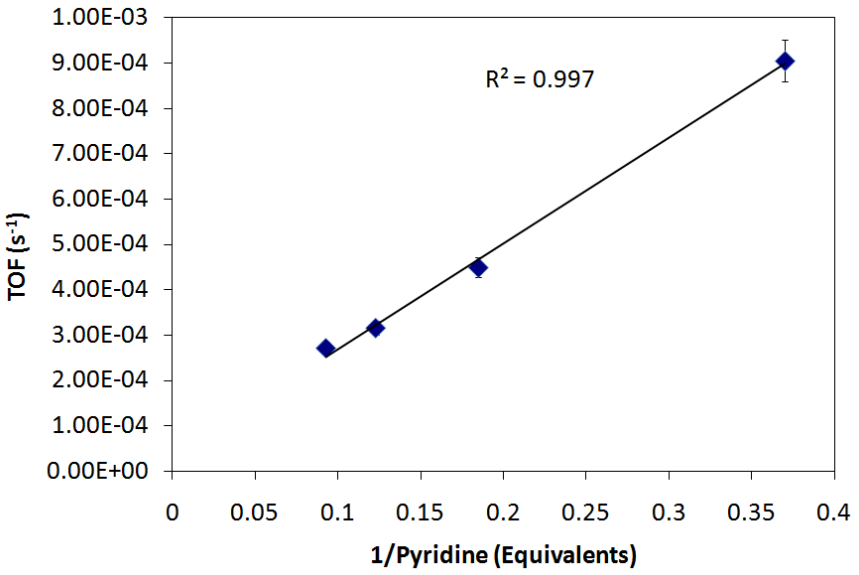

Table S4. TON at various Time (s) for Ph-Ir-Py.

Time (s)	TN
1800	1.9
7200	9.0
14400	19.3

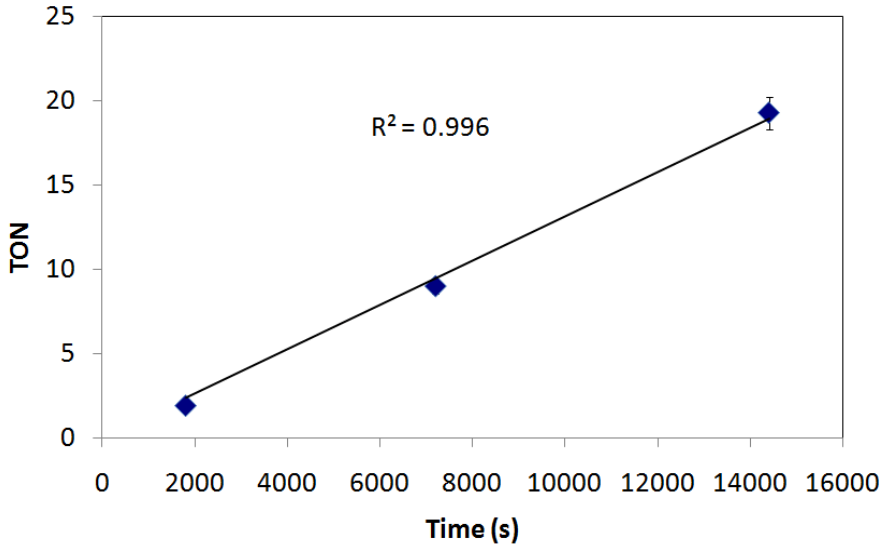

Table S5. Rate difference between Ph-Ir-Py Vs Ph-Ir-H_2O

Time / h	TN (H_2O)	TN (Py)
0	0	0
0.25	14.11	2.3
0.5	14.62	5.21
1	15.13	5.33
1.5	15.3	5.41
2	15.3	5.55

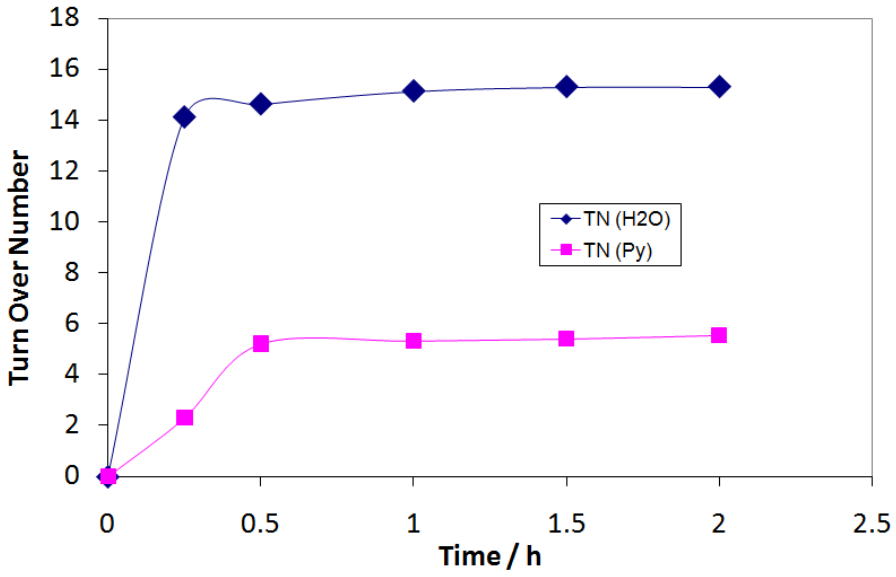

Table S6. Comparison of thermodynamic and experimental ratio for hydroarylation with various olefins.

olefin	-	B3LYP-G	B3LYP-G	dG kcal/mol	exptal	DFT ratio
-	-	A(linear)	B(branched)	-	-	-
propylene	C9H12	-350.13573	-350.134	0.9	61:39	74:36
styrene	C14H14	-541.87036	-541.865	3.2	98:2	97: 03
1-hexene	C12H18	-468.02955	-468.027	1.9	69:31	87: 13
isobutylene	C10H14	-389.43316	-389.428	2.9	82:18	96:4

B3LYP-G values are B3LYP/LACV3P++**//LACVP** gas phase values.

[i] Bennett, M. A.; Mitchell, T. R. B. *Inorg. Chem.* **1976**, 15, 2936.
[ii] Gilman, H., and Brown, R. E., *J. Am. Chem. Soc*. **1929**, 51, 928.